The effect of Mo and V on the hydrothermal crystallisation of hematite from ferrihydrite - an in situ Energy Dispersive X-Ray Diffraction and X-Ray Absorption Spectroscopy study

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Abstract

In this study we used in-situ synchrotron-based energy dispersive X-ray diffraction (EDXRD) to follow the transformation of ferrihydrite to hematite at pH ~ 8 and ionic strength between 0.1 and 0.7. In addition, the effects of co-precipitated molybdenum (Mo) and vanadium (V) on the transformation were evaluated both through EDXRD and X-ray absorption spectroscopy (XAS). The transformation end-product in all experiments was hematite with small amounts of goethite as an intermediate phase. XAS results revealed that Mo and V were initially adsorbed and co-precipitated onto/with ferrihydrite as molybdate and vanadate ions, respectively. After the ferrihydrite transformed to hematite these metals were
sequestered into the hematite structure. The kinetic results showed that the presence of Mo and V in the ferrihydrite structure had little to no effect on the kinetics of the ferrihydrite transformation. The transformation however occurred ~ 30% faster at higher ionic strength.

Introduction

Iron (oxyhydr)oxide mineral phases (e.g., ferrihydrite, FH, Fe5O3(OH)9; goethite, GT, α-FeOOH; hematite, HM, α-Fe2O3) are important components of the iron cycle in many environmental systems, including soils and marine sediments. Furthermore, owing to their high surface areas (up to 700 m² g⁻¹) iron (oxyhydr)oxide phases have a high adsorption capacity for trace elements from solution. They also have a high capacity to take up trace elements via co-precipitation. These properties are important in both natural and contaminated environments as these phases can control the bioavailability of nutrients (e.g., phosphate) and contaminants (e.g., arsenic and lead) in soils, sediments, water columns or waste-water treatment plants. Ferrihydrite is also an important oxidation product in hydrothermal plumes of deep sea hydrothermal vents when acidic, high temperature (350-400°C) fluids containing elevated iron concentration come into contact with seawater (pH = 8.3; ionic strength of ~ 0.7, T = 2-4°C). This process results in hydrothermal vents being a significant source of particulate iron to the global ocean (~ 50 Gg yr⁻¹). Iron oxyhydroxide particulate phases in hydrothermal plumes can scavenge a wide variety of trace elements from seawater (e.g., phosphorus, vanadium, arsenic, molybdenum, lead and rare-earth elements). In addition, during the crystallisation of ferrihydrite, any co-precipitated or adsorbed metals can be either released back into solution or sequestered by the newly formed crystalline phases. Currently, relatively little is known about what controls these processes and it is, therefore, crucial that we understand the availability and fate of trace metals during the formation and crystallisation of iron (oxyhydr) oxide phases.

Molybdenum (Mo) and vanadium (V) are important elements for marine and surface phyto- and zooplankton. For example, Mo catalyses the electron transfer reaction in nitrogen fixation and nitrate reduction, and V is an essential co-factor for enzymatic processes involved in plant growth. In contrast, at high concentrations, both Mo and V, in particular V(V), can become toxic to plants, animals and humans. For example, Mo in concentrations of up to 30 mg L⁻¹ in the diet of sheep inhibits copper uptake in the gastrointestinal tract leading to molybdenosis. V becomes toxic in marine system when its concentrations is above 100 μg
L⁻¹ (6-day LC50 for fish is 0.5-22 mg L⁻¹), whereas V in soils at concentrations of 10 mg kg⁻¹ or more is toxic for terrestrial plants. For humans long term exposure to excess Mo leads to loss of appetite, diarrhea, anaemia and slow growth, whereas V exposure reduces the number of red blood cells, increases blood pressure and even leads to neurological effects.

Furthermore, marine studies have shown that Mo isotopic fractionation in ferromanganese crusts and sediments may be used as a potential proxy for global paleoocean redox conditions. In addition, V/Fe ratios in hydrothermal fractions of marine sediments have been found to be similar to V/Fe ratios in hydrothermal plume particles. These in turn have been found to correlate with dissolved phosphate in seawater, and thus could be useful as a tracer of dissolved phosphate in past oceans.

Ferrihydrite is a metastable and poorly-ordered iron oxyhydroxide phase that is often the first phase to form from solution when dissolved ferric iron hydrolyses. This nanoparticulate phase is thermodynamically unstable with respect to crystalline iron (oxyhydr)oxide phases (e.g., goethite and hematite) under environmental conditions. The kinetics, rate and products of ferrihydrite crystallisation are influenced by a number of factors including pH, temperature, solid/solution ratio and presence of different anions (nitrate, chloride, sulfate and phosphate), or cations (e.g., cadmium, lead and ferrous iron) which can either inhibit or catalyze the crystallisation reactions. pH is one of the primary parameters which influences the kinetics and mechanisms of iron oxyhydroxides' transformation, as it controls the surface properties of the particles (e.g., surface charge) and speciation/concentration of ions in the reacting solutions. Extensive studies have been carried out on ferrihydrite crystallisation as a function of pH and temperature (room temperature to > 200°C), at low ionic strength conditions. Overall, the transformation of ferrihydrite to hematite/goethite is controlled by the pH-dependent solubility of ferric iron. Hematite is the dominant end-product at near neutral pH where iron solubility is lowest, where the transformation occurs via the aggregation of ferrihydrite particles followed by a dehydration/recrystallisation process. In contrast, at both acidic and alkaline pH (i.e. 2–5 and 10–14), ferric iron solubility is higher and goethite is the dominant end-product forming via a dissolution and re-precipitation mechanism. These conclusions have been drawn from, for example, studies by Schwertmann and Murad and Schwertmann et al. who showed that at pH values of 7-8, close to the point of zero charge (PZC) of ferrihydrite, hematite is the favored end product. At low temperatures and alkaline pH (>10-11) goethite is the favored end-product, although at high temperature goethite is an intermediate phase and hematite is the main final end product. Ionic strength is another parameter which has a complex...
influence on solubility\textsuperscript{44} and consequently mineral nucleation and growth\textsuperscript{1, 45, 46}. Due to the complexity of the various mineral formation mechanisms and the related effects of various chemical parameters (e.g. pH, solution saturation\textsuperscript{47}, presence of other competitive ions, size of seeding crystal\textsuperscript{45}) on each specific process, these trends cannot be generalized and thus there is a need for them to be studied individually.

There are a limited number of studies of Mo or V uptake via adsorption onto ferrihydrite\textsuperscript{19, 48-50} and its fate during crystallisation. We are also not aware of any studies which investigated the co-precipitation of Mo or V with ferrihydrite and their effect and fate upon its crystallisation at near neutral pH. Thus, this research focused on: (i) evaluating the partitioning of Mo and V, which have been adsorbed onto or co-precipitated with ferrihydrite, during transformation to hematite; (ii) assessing local bonding environments of Mo and V when adsorbed and co-precipitated with ferrihydrite (initial material), and hematite (the final end-product) using X-ray absorption spectroscopy (XAS), and (iii) determining the effect of high temperature, high ionic strength and the presence of Mo and V on the kinetics of ferrihydrite crystallisation to hematite at pH 8 using \textit{in-situ} synchrotron-based energy dispersive X-ray diffraction (EDXRD).

\textbf{Methodology}

\textbf{Pure ferrihydrite synthesis - starting materials}

Pure 2-line ferrihydrite was synthesized following the method of Cornell and Schwertmann\textsuperscript{51} by slow titration of a 0.127 M Fe (NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O solution with a 1.0 M sodium hydroxide solution. The obtained slurry was washed 5 times with distilled water in consecutive dispersion and centrifugation cycles, until the concentration of total dissolved solids in the slurry was less than 20 mg L\textsuperscript{-1} (measured using a Hanna DiST1 TDS meter). The density of the washed ferrihydrite slurry was determined from the weight ratio of triplicate subsamples measured before and after drying at 50°C for 16 hours. The slurry was stored in a fridge (4°C) for a maximum of one week prior to use in the metal adsorption and transformation experiments.

\textbf{Ferrihydrite transformation: microscopy and XRD}
Ex-situ test batch experiments were carried out at 160°C and 200°C using a pure FH slurry (14g dry FH L⁻¹, IS of 0.01 (to mimic fresh water conditions) and 0.7 (to mimic seawater conditions) at near neutral pH (initial pH was 8), without in situ EDXRD data collection. The ionic strength was adjusted using a 1M NaCl solution. The experiments were conducted in Teflonlined Parr® steel hydrothermal reactors (total volume of 20 mL). Experiments carried out at the Synchrotron Radiation Source (SRS, T ≤ 200ºC were controlled by a heating block fitted with four heating cartridges and a thermocouple to ensure a constant temperature during the experiments) were up to 8 hours and experiments carried out at the University of Leeds (in the oven, at 160ºC) were up to 24 hours).

At select time points during the experiments, the reactions were quenched and the solids were separated from the supernatants, washed by MQ water and analysed by high-resolution field emission gun transmission electron microscopy (HR-FEG-TEM, Philips/FEICM200) operated at 197 keV and fitted with an energy dispersive X-ray spectrometer (EDS). The initial, intermediary and end-product solids were analysed using a conventional X-ray diffractometer (Philips PW 1730/10, CuKα, λ=1.54Å). Changes in the pH were monitored at the beginning and the end of the experiments. Ferrihydrite dissolution was quantified by measuring the dissolved iron concentration (using the Ferozzine method⁵¹) in the supernatant at the end of the experiments.

**Partitioning of Mo/V during ferrihydrite transformation**

(i) Adsorption and co-precipitation experiments

Mo and V adsorption experiments were carried out in 500 mL batch reactors at pH 7, The concentration of FH was 2 g L⁻¹ and the initial concentration of Mo/V were 1000 µM. The pH was checked throughout the adsorption experiments and adjusted to a constant value with 0.01M NaOH or 0.01M HCl when needed. The adsorption experiments were run for 24 hours as sacrificial replicates to ensure that there was always enough solid material for evaluating the ferrihydrite transformation products both after adsorption and at the end of the transformation experiment, including desorption post transformation. The amount of Mo and V adsorbed onto ferrihydrite was calculated from the mass balance, as the difference between the initial added and post adsorption metal values measured in the supernatant by inductively coupled plasma optical emission spectrometry (Perkin Elmer Optima ICP-OES).

Ferrihydrite co-precipitated with Mo (Mo-FH) and V (V-FH) were prepared by synthesizing batches of ca. 10 g FH in ca. 800 mL of solution in the presence of 1000 µM
Mo/V. Mo solution were made from Na$_2$MoO$_4$·2H$_2$O, VWR BDH AnalaR, 99.5% (added to the basic solution of synthesis) and vanadium from Na$_3$VO$_4$, Sigma Aldrich, 99.98% (added to the ferric solution prior to mixing). The Mo and V content in the resulting ferrihydrite samples were determined by mass balance of Mo and V initial added and final measured in the co-precipitated slurry supernatant (after filtration through 0.2 µm filters) measured via ICP-OES. For each co-precipitated ferrihydrite batch the density was determined by dry weight (in triplicate, at 50ºC, for 16 h). After washing by MQ water the resulting slurries had densities of 0.041 g FH g$^{-1}$ slurry (for Mo-FH) and 0.042 g FH g$^{-1}$ slurry (for V-FH). These slurries were stored in the dark, at 4ºC and pH 7 for maximum of 1 week prior to initiating the off-line transformation experiments.

(ii) Off-line transformation experiments

The freshly-made Mo/V-adsorbed and co-precipitated ferrihydrite slurries were transformed to hematite at 150 ºC and pH 8 in Teflon lined Parr® steel hydrothermal reactors (in a Binder FP series oven) for ~2 days. For transformation experiments 0.25 g FH was added to 10 ml of solution in Teflon lined Parr® steel hydrothermal reactors, leading to a ferrihydrite concentration in transformation experiments of 25 g dry FH L$^{-1}$. The transformed samples were centrifuged at 8000 rpm for 15 minutes to separate the solid from the supernatant and the transformation end-product solids was analysed by XRD while the supernatant solutions were filtered through 0.2 µm acetate cellulose syringe filter and acidified for the analysis of Mo and V by ICP-OES.

(iii) Desorption experiments

A desorption step was used to quantify the amount of Mo or V associated with the hematite surface after the transformation$^{53}$. Sacrificial replicates of the post-transformation samples were centrifuged and the separated solids were equilibrated under constant stirring conditions with a 2 M NH$_4$OH solution (0.25 g solids/10 mL, pH >11) for 30 minutes (a short time to avoid/minimize iron oxyhydroxides dissolution, but sufficient for surface desorption to take place). The supernatant was collected by centrifugation, filtered and analysed for Mo and V concentrations by ICP-OES. The remaining hematite was digested in 6 M HCl and the resulting solution was analysed by ICP-OES to quantify Mo and V contents within the mineral particles (structure).

Bonding environment of Mo and V associated with co-precipitated ferrihydrite and hematite: XAS study
Synchrotron-based X-ray absorption spectroscopy (XAS) was used to investigate the bonding environment of Mo and V associated with (i) ferrihydrite (Mo/V ads FH or Mo/V copp FH); (ii) hematite as end-product from ferrihydrite transformation (Mo/V ads FH -tr or Mo/V copp FH- tr) and (iii) the hematite after the desorption step (Mo/V ads FH-tr-des or Mo/V copp FH-tr-des). The adsorption, co-precipitation, off-line transformation and desorption processes were carried out as described above at temperatures between 160-200 °C and at a pH of 7. For the Mo system two extra sets of experiments were considered: a) adsorption and co-precipitation experiments with different initial Mo concentrations in solutions: 1, 10, 100, 1000 µM (and 1g FH L⁻¹ at pH 7 and T=30°C) to evaluate whether Mo forms specific Mo phases/clusters/polymers; and (b) adsorbed and co-precipitated samples with 1000 µM Mo transformed at pH 7 and at pH 8.5 at the same temperature (T = 150°C) to assess whether the initial transformation pH influenced the bonding environment of Mo in the hematite end-product. In the results XAS samples will be named using initial Mo/V concentration used in experiment (i.e., Ads/ Copp 1/10/100/1000 µM Mo/V).

XAS measurements were carried out at the Synchrotron Radiation Source (SRS), at the Daresbury Laboratory at station 16.5 for Mo and at the Diamond Light Source (DLS), at the I18 microfocus spectroscopy beamline for V. Station 16.5 was equipped with a water-cooled Si (220) double crystal monochromator (DCM) and a 30 element monolithic Ge fluorescence solid state detector. Harmonic rejection was achieved by use of a plane mirror. In contrast station I18 is equipped with a cryo-cooled (Si 111) DCM, and a 9 element Ge detector; harmonic rejection was achieved using a Si stripe on one of the micro-focusing mirrors, which was defocused for this experiment. Data was collected from the Mo ferrihydrite samples using a liquid nitrogen cooled cryostat at 80K, whereas data was collected from the V samples at room temperature. Two regimes were considered from the XAS spectra: X-ray absorption near edge structure (XANES) and extended X-ray fine structure (EXAFS). The interpretation of the XANES gives information about the oxidation state and coordination chemistry of the absorbing atom, while EXAFS is used to determine bond and inter-atomic distances, coordination number and species of the neighbors of the absorbing atom. Samples from the co-precipitation and adsorption experiments containing Mo/V in the initial system from 1 to 1000 µM were examined in fluorescence mode, while the standards were run in transmission mode. Synthetic and natural standards (Na₂MoO₄; K₂MoO₄ and MoO₃ for molybdenum and Na₃VO₄ and V₂O₅ for vanadium) were analysed. Where necessary the standards were diluted appropriately with an inert diluting salt, boron nitride. All standards were analysed by conventional XRD to confirm their identity and purity.
Data normalization and linear combination analysis were done using the Athena software. EXAFS data fitting, with coordination numbers as integer numbers, was carried out using the Artemis software using Feff 6. Athena and Artemis are both part of Demeter package. The goodness of EXAFS data fitting is given by R factor, which represents the absolute misfit between the theory and the data.

Transformation kinetics: Energy Dispersive X-Ray Diffraction

(i) On-line, in situ, transformation experiments

Time-resolved EDXRD measurements were performed at SRS Daresbury Laboratory on station 16.4. The use of EDXRD allows for monitoring of changes in diffraction intensities during in situ and time resolved crystallisation experiments in solution. For this, a polychromatic X-ray beam was directed towards the sample (15 mL of a 50 gL\(^{-1}\) ferrihydrite slurry at pH 8) contained in a Teflon-lined steel hydrothermal reactor. For the pure FH, Mo-FH and V-FH systems, experiments were carried out at an ionic strength (IS) of 0.7 (adjusted with 1M NaCl) and at temperatures between 130ºC to 240ºC. For the Mo-FH system an experiment was also carried out at IS = 0.1 at 160ºC. The reaction cells were isothermally equilibrated at a constant temperature and the contents stirred via a magnetic stirring incorporated within the heater housing of the reaction system. The diffracted beam was detected by three solid detectors. Further details about similar in-situ experiments, the station set up and data acquisition can be found in Shaw et al. and Davidson et al. Experiments were conducted for between 10 and 160 minutes, with diffraction patterns recorded every minute. Initial and final pH values (measured with a ORION 710A pH meter) as well as iron concentrations (analysed by Ferrozine) in the filtered final solutions were also measured. Upon completion of each experiment the solid end-products were separated by filtration, washed and analysed with a conventional XRD to check for possible minor phases not detectable by EDXRD. The progress of the crystallisation reaction was evaluated through the change in the normalised area of the Bragg peaks of hematite (and goethite) calculated using XFIT and expressed as:

\[ \alpha = \frac{(A_t - A_{\min})}{(A_{\max} - A_{\min})} \]  

where \( \alpha \) is the degree of reaction, \( A_t \) is the peak area at time \( t \), \( A_{\min} \) is the minimum (time at which the Bragg peak first appeared) and \( A_{\max} \) was the maximum peak area. The (110) peaks for hematite and goethite were chosen as they are distinct and high intensity peaks that clearly differentiate hematite from goethite in mixed phase samples.

(ii) Kinetic evaluation and activation energies
The growth of (110) Bragg peaks from the EDXRD data was fitted with the Johnson–Mehl-Avrami-Kolmogorov (JMAK) kinetic model\(^{60-62}\) to obtain kinetic parameters of the ferrihydrite transformation to hematite

\[
\alpha = 1 - e^{-k(t-t_0)^m}
\]  

(2)

where \(k\) is the rate constant for the reaction (s\(^{-1}\)), \(t\) is time (s), \(t_0\) is the induction time (s) and \(m\) is a constant that depends on the reaction mechanism and the dimensionality of growth \(^{63}\). The fits were performed in Origin\(^{®}\) \(^8\) \(^{64}\). Indeed several other kinetic models for phase transformations are available in the literature\(^{65, 66}\) and were considered. However, the JMAK model was selected due to its simplicity and popularity, and because it describes our data best (see below).

The apparent activation energies of crystallisation of the end-products were calculated from the Arrhenius equation:

\[
k = A \cdot e^{-\frac{E_a}{RT}}
\]  

(3)

where \(k\) is the rate constant; \(A\) is the frequency or pre-exponential factor; \(E_a\) is the activation energy (kJ mol\(^{-1}\)), \(R\) is the gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)) and \(T\) is the absolute temperature in K. For comparison the “time to a given fraction method”\(^{67}\), was also used to determine the activation energy of crystallisation. This approach relies solely on the time to a given fraction of transformation \((t^*)\) as a function of temperature and can be expressed as:

\[
\ln t^* = \text{const.} - \ln A + \left( \frac{E_a}{R} \right)(1/T)
\]  

(4)

where the \(t^*\) is the time of the given fractionation which was chosen (usually, 50% transformation), in seconds.

Results and discussions

Ferrihydrite transformation to hematite at neutral pH

High-resolution TEM images were collected from the ferrihydrite starting materials, intermediate reaction stage samples and the reaction end-products (Figure 1.A-C) from the ex-situ experiment with pure ferrihydrite reacted at 160°C. Images of the starting material showed that ferrihydrite consisted of aggregated nanoparticles < 5nm in size, which is in agreement with previous TEM observation of 2-line ferrihydrite\(^{68}\). After a few hours, the slurry consisted of a mixture of 2-line ferrihydrite nanoparticles and hexagonal hematite plates, with minor quantities of goethite (small marked needles in Figure 1.B). Finally, the end-product was pure hematite (Figure 1.C) consisting of hexagonal platelets of varying size.
Figure 1. Representative FEG-TEM images of: (A) the starting material, ferrihydrite (FH), (B) intermediate phases consisting of hematite, ferrihydrite and minor goethite (GT) as intermediate and (C) end product, hematite (HM) from the ex-situ, pure ferrihydrite transformation experiment at T=160ºC;

Off-line XRD results from this transformation experiment (Figure SI 1), supported by TEM data, are in good agreement with literature studies of hematite crystallisation from ferrihydrite under near neutral pH conditions\textsuperscript{37, 40}. Measurements of pH at the end of experiments showed a decrease in pH (~6) and no dissolved iron (<0.001 mg L\textsuperscript{-1}) in the supernatant.

Partitioning of V and Mo during and after ferrihydrite transformation

Table 1 summaries the three different metal pools: solution (in supernatant solution after transformation), surface (release after desorption) and structure (retained in the hematite structure after desorption) for V and Mo associated with the iron (oxyhydro)oxides.

The partitioning data for the Mo co-precipitated ferrihydrite experiment revealed that only ~ 3% of the Mo remained in the reacting solution after the transformation and ~ 3% of the total Mo was bound to the surface of the hematite, with the remaining >94% structurally incorporated. Interestingly, all V that was co-precipitated with the initial ferrihydrite became incorporated into structure of the hematite end-product. For the adsorption experiments the partitioning results showed that ca. 4% of Mo and 0% of V remained in the solution after the transformation ~6% of Mo and 4% of V was bond to the surface and 90% of Mo and 96% of V were structurally incorporated.
Table 1. Partitioning of V and Mo adsorbed onto and co-precipitated with ferrihydrite and after ferrihydrite transformation to hematite (initial pH 7, initial Mo/V concentration 1000µM).

<table>
<thead>
<tr>
<th>Partitioning / uptake pool</th>
<th>Adsorption</th>
<th>Co-precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
<td>V</td>
</tr>
<tr>
<td>% in solution</td>
<td>3.5</td>
<td>0.0</td>
</tr>
<tr>
<td>% on surface (i.e., adsorption)</td>
<td>6.4</td>
<td>4.1</td>
</tr>
<tr>
<td>% structurally incorporated</td>
<td>90.1</td>
<td>95.9</td>
</tr>
</tbody>
</table>

The majority of the Mo and V in both systems (via co-precipitation and via adsorption) became sequestered in the end-product structure.

Bonding environment of Mo and V associated with co-precipitated ferrihydrite and hematite: XAS

The Mo X-ray absorption spectra of the ferrihydrite co-precipitated and adsorbed with various Mo concentrations showed no differences indicating that Mo did not polymerize or form specific precipitates in these systems and that its bonding environment was alike over the range of concentrations used (see Figure SI 5 for EXAFS spectra as example). Thus, only samples from the highest working concentrations are discussed below.

Mo XAS

Figure 2 displays K-edge Mo- X-ray absorption near-edge structure (XANES) profiles of the adsorbed (Figure 2.A) and co-precipitated (Figure 2.B) samples and the appropriate standards (i.e., Na₂MoO₄ and MoO₃).
Figure 2. Mo K edge XANES spectra for adsorption samples (A), and co-precipitated samples (B) and standards

The Mo K-edge XANES spectra for both Mo-adsorbed ferrihydrite and Mo co-precipitation ferrihydrite are alike and very similar to the spectrum of the Na$_2$MoO$_4$ standard: with pre edge feature at 20002 eV, adsorption edge at 20015 eV and the top of the white line at 20040 eV, respectively. The XRD also confirmed that in the Mo adsorbed and co-precipitated ferrihydrite samples no other Mo mineral phases formed. The lower intensity of the pre-edge feature in samples compared with standard may indicate some structural disorder in the Mo adsorbed and co-precipitated samples. In general, Mo K edge XANES results suggest that Mo (VI) is largely taken up into ferrihydrite as the molybdate species, that it is tetrahedrally-coordinated, both in the adsorption and co-precipitation systems. For the Mo adsorbed onto ferrihydrite samples this matches well previous findings$^{19,20,69}$.

The post transformation samples have different XANES spectra compared with Mo ferrihydrite samples: in particular, the peak of the white line is shifted by $\sim$ -5 eV and the pre edge peak (at 20003 eV) is much less pronounced. These differences may suggest that Mo (VI) has adopted a distorted octahedral geometry (seen in MoO$_3$ standard), in the post transformation hematite samples.
Figure 3. Summary of $k^3$ weighted Mo-K edge EXAFS spectra (A and C) and phase corrected Fourier-Transforms (B and D) for EXAFS spectra for adsorbed (A and B) and co-precipitated (C and D) samples and Na$_2$MoO$_4$ standard.

For the freshly adsorbed and co-precipitated ferrihydrite samples the Mo $k^3$ weighted EXAFS and Fourier transformed fitting results are in good agreement with our interpretation of the Mo K-edge XANES. The Mo $k^3$ weighted EXAFS plots (Figure 3 A and C) show similar amplitudes shape for the freshly Mo adsorbed and co-precipitated ferrihydrtes and Na$_2$MoO$_4$ standard, but with different intensities. Fits of the adsorbed (Figure 3 A) and co-precipitated (Figure 3 C) indicate that there are four oxygen atoms situated in the first shell at a bond distance of 1.76 Å from the main Mo atom. This is indicative of tetrahedrally coordinated Mo in molybdate, which agrees with previous literature findings that reported that Mo adsorbs as an outer sphere molybdate species onto ferrihydrite surfaces$^{19, 20, 70}$ (Table 2). The differences in
the intensities for the adsorbed and co-precipitated samples are correlated with the variations in the $\sigma^2$ factors and indicate different degrees of disorder for the molybdate species associated with the ferrihydrite structure.

As the Mo-XANES suggests that Mo may be octahedrally coordinated in the transformed samples an attempt was made to fit our Mo post transformation spectra to a model in which Mo substitutes for the octahedral iron in hematite. The results together with hematite structural data from Wolska and Schwertmann$^{71}$ are presented in Table 2. The hematite structure is formed of a succession of oxygen octahedra (with the Fe (III) ions residing inside) and empty tetrahedral interstitial sites. There are various Fe-Fe distance in the hematite structure corresponding to different octahedral linkages: 3.70 Å and 3.34 Å specific to double corner sharing octahedra; 2.97 Å specific to edge sharing octahedra and 2.89 Å specific to face sharing octahedral sites. In hematite Fe has two shells of three oxygen atoms at distances of 1.94 Å and 2.11Å, respectively (Table 2).
**Table 2.** Summary of Mo EXAFS fits parameters and crystallographic information of appropriate standards.

<table>
<thead>
<tr>
<th>sample</th>
<th>Path</th>
<th>Path Degeneracy</th>
<th>Bond distance R (Å)</th>
<th>σ² #</th>
<th>R-factor%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂MoO₄</td>
<td>Mo-O</td>
<td>4</td>
<td>1.76±0.01</td>
<td>0.001±0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>Na₂MoO₄*</td>
<td>Mo-O</td>
<td>4</td>
<td>1.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoO₃⁺</td>
<td>Mo-O</td>
<td>2</td>
<td>1.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo-O</td>
<td>2</td>
<td>1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo-O</td>
<td>2</td>
<td>2.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoO₃⁻</td>
<td>Mo-O</td>
<td>2</td>
<td>1.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>1.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo ads FH, pH7</td>
<td>Mo-O</td>
<td>4</td>
<td>1.76±0.01</td>
<td>0.03±0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>Mo ads FH tr, pH7</td>
<td>Mo-O</td>
<td>2</td>
<td>1.74±0.07</td>
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<td>Mo-Fe</td>
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<td>Fe-Fe</td>
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<td>Mo-Fe</td>
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<td>Mo copp FH tr, pH 8.5</td>
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<td></td>
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<td>3</td>
<td>3.08±0.02</td>
<td>3.44±0.11</td>
<td>0.007±0.003</td>
</tr>
</tbody>
</table>

1. *Na₂MoO₄* structure (ICSD 4156) after Matsumoto et. al.,[70]
2. *MoO₃* structure after, Radhakrishnan et. al.[72]
3. *MoO₃* structure of MoO₃ standard refine from XAFS data using Excurv98, Brinza 2010
4. *Hematite* structure (ICSD 56369) after Wolska and Schwertmann.[71]
5. *σ²* - the mean-square disorder in the distribution of interatomic distances, Ravel and Newville, 2005.[56]
6. *R*-factor-sum of the residual: a measure of the percentage misfit between the data and theory. Ravel and Newville, 2005.[56]

All adsorbed samples post transformation (and desorption) fitted well to a model comprising of two oxygen distances in the first coordination sphere: two oxygen atoms at 1.74 Å - 1.76 Å and three oxygen atoms at 1.97 Å-1.99 Å. There are three Fe shells at distances varying from 2.89 Å - 2.96 Å; 3.06 Å - 3.09 Å and 3.45 Å - 3.53 Å. When the coordination number (5 for the O shell) and inter atomic distances (smaller) of the Mo-O/Fe shells in the Mo associated hematite samples is compared with Fe-O distances in pure hematite it suggests that Mo in our samples was mainly accommodated in octahedral sites of the hematite structure. Further, iron shells with varying interatomic distances compared to pure hematite may indicate different substitution degrees of Mo in the hematite structure.

For the co-precipitated and transformed samples, larger interatomic distances for oxygen in the first and second shells at 1.79/80 Å and 2.05 Å as well as bigger iron interatomic distances at 2.94/8 Å and 3.08/9 Å and 3.44/8 Å may indicate possible distortions of the Mo octahedrons within the hematite structure (or a mixture of Mo occupied Fe octahedral sites in hematite). Variable *σ²* factors of the fits and well as different interatomic distance errors (i.e., slightly larger for the first and third iron shells) among the co-precipitated samples support such distortions (and/or heterogenous Fe occupancy by Mo) which are well known to be encountered in high pressure samples with transition metals in octahedral symmetries.[73] Bond valence sum analyses confirmed that Mo can exist in six-coordinated geometries with the bond distances modeled for the co-precipitated post transformed samples.[74]

There are several factors that could contribute to local distortions of the polyhedra. These include: fast dehydration and rearrangement of ferrihydrite, high temperature (up to 200°C) and pressure (not measured) of the reactions, differences in Fe (0.64 Å) and Mo (0.59 Å) ionic radii and different degrees of Mo substitution within the hematite structure. In addition, the initial transformation pH (i.e., 7 and 8.5) does not appear to influence the Mo speciation in the end product (Figure 4).
**V - XAS**

The V K-edge XANES spectra for V adsorbed onto and co-precipitated with ferrihydrite are similar to the Na$_3$VO$_4$ standard spectra and feature a pre edge peak at about 5649.5 eV and a shoulder at 5474.9 eV (Figure 4 A and B). Comparison of the V K-edge XANES of the standard with the adsorbed and co-precipitated samples suggests that V is present as V (V) and is tetrahedrally coordinated.

![Figure 4. V K edge XANES spectra for adsorption samples (A) and co-precipitated samples (B) and Na$_3$VO$_4$ standards.](image)

The lower intensity (ca. 60%) of pre edge peak at 5470 eV of V K-edge XANES of the transformed co-precipitated samples compared with the pre-transformed samples or the Na$_3$VO$_4$ standard (but also higher than in V K-edge XANES spectrum of a V(III) specie, i.e. V$_2$O$_3$, and V(IV) specie such as V$_4$O$_7$) indicate a change in the structural geometry of V in the hematite structure, possibly to octahedrally coordinated. Comparing our XANES spectra with XANES profiles of relevant V oxide compounds studied by Wong et al., it can be seen that the position of the pre edge peak in the transformed sample spectrum (5468.6 eV) is quite similar to the pre edge features of V$_2$O$_4$ (IV) (5469.7 eV using our calibration value for V foil of 5464.3 eV). This indicates that V could have been at least partially reduced to V(IV) during the transformation reaction, possibly due limited O$_2$ concentration in the transformation chamber.
Figure 5. Summary of $k^3$ weighted V-EXAFS spectra (A) and calculated Fourier-Transforms (B) for EXAFS spectra for co-precipitated and adsorbed samples and Na$_3$VO$_4$ standard.

The EXAFS of V adsorbed onto and co-precipitated with ferrihydrite and the standard Na$_3$VO$_4$ showed similar features (Figure 5). The best fitting parameters give V-O bond distances of 1.68 Å and 1.70 Å, which are typical of a tetrahedrally coordinated vanadate species. The V-O distance found in VO$_4$ tetrahedral varies between 1.65 - 1.76 Å, as a function of the neighboring metals in each specific compounds and their structural geometry (i.e., MnNa(VO$_4$)$_2$; NaCaVO$_4$; Cd$_4$ Na (V O$_4$)$_3$). These EXAFS fitting results indicate that V is adsorbed and co-precipitated as vanadate onto the surface of ferrihydrite and within the ferrihydrite structure (Table 3).

### Table 3. Summary of V EXAFS data fits and appropriate standards

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bond type</th>
<th>Coordination number</th>
<th>Inter atomic distance, $R$ (Å)</th>
<th>$\sigma^2$ factor *</th>
<th>R-factor ~</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_3$VO$_4$</td>
<td>V-O</td>
<td>4</td>
<td>1.70±0.02</td>
<td>0.003±0.004</td>
<td>0.01</td>
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<tr>
<td>Na$_3$VO$_4$ 3H$_2$O</td>
<td>V-O</td>
<td>3</td>
<td>1.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>V ads FH, pH7</td>
<td>V-O</td>
<td>4</td>
<td>1.70±0.02</td>
<td>0.002±0.004</td>
<td>0.02</td>
</tr>
<tr>
<td>V copp FH, pH7</td>
<td>V-O</td>
<td>4</td>
<td>1.68±0.02</td>
<td>0.004±0.003</td>
<td>0.009</td>
</tr>
</tbody>
</table>

*Na$_3$VO$_4$ 3 H$_2$O structure (ICSD 62533) after Kato and Takayama-Muromachi.

*$\sigma^2$ - the mean-square disorder in the distribution of interatomic distances, Ravel and Newville, 2005

~ R-factor-sum of the residual: a measure of the percentage misfit between the data and theory. Ravel and Newville, 2005
Differences in amplitudes of the $k^3$-weighted EXAFS and in the intensity of the first peak in Fourier transform between the Na$_3$VO$_4$ standard and the adsorbed and co-precipitated samples possibly indicate different degrees of hydration or various scattering effects from the neighbouring atoms in the V tetrahedral structure. The Fourier transform of the V adsorbed ferrihydrite EXAFS displays a broad peak at 2.97 Å and that of the co-precipitated ferrihydrite displays a second peak at 2.40 Å and a third broad peak at a distance of 2.98 Å. No sensible model could be built that fitted these peaks successfully. However these peaks might result from various V-Fe scattering paths from possible inner-sphere surface complexes on ferrihydrite$^{2,9}$.

Modeling V in the Fe site in hematite did not refine to a sensible set of parameters or a good fit. Thus we can only conclude that V XANES, as V EXAFS tell us little about the incorporation mode of V in the hematite structure, other than that there are probably a mixture of different sites, some of which are octahedral (see the data in Figure SI 7).

**Transformation kinetics: Energy Dispersive X-Ray Diffraction**

**Pure ferrihydrite transformation at pH 8 and ionic strength 0.7**

The growth of the hematite (110) and goethite (110) diffraction peaks at all temperatures as a function of time is shown in Figure 6 and Figure SI 2. In all the on-line, in-situ transformation experiments carried out at temperatures > 140°C the diffraction patterns showed that hematite is the main transformation end product. The EDXRD data collected from the experiment run at temperatures 140°C revealed that minor amounts of goethite were present during the transformation (Figure SI 2). Differently, goethite was observed as an intermediate (minor amount) in the off-line ex-situ experiments at 160°C (Figure SI 1). This is likely due to the EDXRD spectra being collected from solids suspended in solution, though this is one of the advantages of the EDXRD technique, it leads to a high background in the in situ EDXRD spectra$^{57}$. The high background may have masked minor phases (i.e., goethite).

The EDXRD data revealed that the degree of ferrihydrite transformation to hematite is temperature dependent (Figure 6, and Figure 7A and B). The induction time, for the appearance of hematite, decreases with increasing temperature, whereas the rate of crystallisation increases with increasing temperature (Table 4). Specifically, in the pure-ferrihydrite system at 240ºC, the (110) peak of hematite was first observed after 8 minutes and the reaction was complete after 15 minutes, while at lower temperature (130ºC) hematite
started to form only after 40 minutes and the reaction was complete only after ~100 minutes (Figure 6).

![Figure 6. The degree of transformation of pure ferrihydrite to hematite as a function of temperature in the in situ EDXRD experiments](image)

**Figure 6.** The degree of transformation of pure ferrihydrite to hematite as a function of temperature in the *in situ* EDXRD experiments

**The effect of co-precipitated Mo and V on the ferrihydrite**

The analyses of supernatant from the Mo and V co-precipitated ferrihydrite experiments revealed that the starting materials used in the *in-situ* transformation experiments contain ~3.1 mg Mo g⁻¹ and 1.6 mg V g⁻¹ (or ~0.03 mM Mo/V g⁻¹). The EDXRD results showed that the presence of Mo and V (in co-precipitated ferrihydrite, Figure 7A and B) increased the induction time of the transformations, compared to pure FH system (Figure 6) at the same ionic strength (0.7) and temperature (160ºC as example). This effect could be observed clearly at low temperature (i.e., 140ºC) at which the induction time increased by up to 32% and 38% in the Mo-FH and V-FH system, respectively (Figure 7.C and 7.B, and Table 4). However, at higher temperatures (above 220ºC), this increase was not observed; possibly because the reaction was too rapid or the influence of temperature outweighed the influence of the metals.
Figure 7. The degree of transformation of ferrihydrite to hematite as a function of time, temperature and ionic strength for: (A) Mo-FH at IS=0.7; (B) V-FH at IS=0.7; (C) pure FH and Mo-FH at 160°C and IS=0.7; (D) Mo-FH at 160°C and IS=0.7 and IS=0.1. Symbols are experimental data points and lines represent the JMAK fits.

Comparison of the reaction rates in the Mo system at high (0.7) and low (0.1) ionic strengths (Figure 7D) revealed that lowering the ionic strength retards the ferrihydrite transformation to hematite. For example, at 160°C and higher ionic strength the induction time of the transformation was reduced from 32 minute to 23 minutes (i.e., about 30%; Figure 7.D).

Fitting the degree of the transformation of ferrihydrite vs. time with the JMAK model yielded values (Table 4) for rate constant ($k$), induction time ($t_0$) and exponential factor ($m$). The results shows that in all three systems studied, the hematite crystallisation rate increases with temperature, while the induction times decreases with increasing temperature.
Table 4. JMAK fitting parameters (with to fixed as given by the experimental data) and activation energies for hematite formation with and without Mo and V for the experiments at IS=0.7

<table>
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<tr>
<th>Temp (°C)</th>
<th>k *10^-4 (s^-1)</th>
<th>t₀ (s)</th>
<th>m</th>
<th>R²</th>
<th>Temp (°C)</th>
<th>k *10^-4 (s^-1)</th>
<th>t₀ (s)</th>
<th>m</th>
<th>R²</th>
<th>Temp (°C)</th>
<th>k *10^-4 (s^-1)</th>
<th>t₀ (s)</th>
<th>m</th>
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<td>240</td>
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<tr>
<td>140</td>
<td>6.8±0.3</td>
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<table>
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<tr>
<th>Ea crys.AA (kJ/mol)</th>
<th>33 (±6)</th>
<th>36 (±7)</th>
<th>31 (±8)</th>
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</table>

* only the beginning of the transformation was recorded for this experiment.
‡ $E_a$ crys.TGF is the apparent activation energy of crystallisation derived using ‘Time to a given fraction” method for t=50%.
* fixed values
The $m$ values obtained from the JMAK fits (Table 4), ranged between 2-3. The classification by Hulbert\textsuperscript{63} for $m$ values indicate that values of 2-3 are suggestive of 2D phase boundary controlled growth. Thus, our values supports the two dimensional growth of the hematite plates.

Using the Arrhenius approach the apparent activation energies of crystallisation for hematite for all systems were derived but show that Mo and V (at all concentrations) did not have any significant effect on the crystallisation activation energy (Table 4), relative to pure ferrihydrite system. Shaw et al.,\textsuperscript{33} calculated, via the Arrhenius approach, an activation energy for hematite crystallisation at pH 10.7 of 69 ($\pm$6) kJ mol$^{-1}$. This higher value for hematite formation under alkaline conditions compared with the values obtained in the present study (38 $\pm$8; Table 4) can be explained by the difference in pH i.e., alkaline vs. near neutral conditions, 2.7 pH unit difference\textsuperscript{11, 32, 33, 42, 80, 81}.

The apparent activation energies of crystallisation to hematite ($E_{a{\text{cryst, TGF}}}$, Table 4) calculated using the “time to a given fraction” (TGF) approach\textsuperscript{67} resulted in comparable values to those obtained from the Arrhenius approach. Thus, using this approach we recalculated the crystallisation activation energy of goethite (without phosphate) from Shaw et al.,\textsuperscript{33} using the “time to a given fraction’ approach\textsuperscript{67}, and obtained a very good agreement (67 $\pm$4 kJ mol$^{-1}$) with the activation energy calculated via the Arrhenius approach, again indicating that this approach can be applied to extrapolate and calculate activation energies for mineral crystallisations at different temperatures.

Using the dependence of rate constant and the induction time on temperature (i.e., the Arrhenius plots obtained in the in-situ experiments, Figure SI 3 and Figure SI 4), extrapolations can be used to calculate the time frame for ferrihydrite transformation (and metals sequestration) at low temperatures. This approach can be used to calculate time frames for metal sequestration by iron (oxyhydr)oxides in soils, sediments and marine systems (i.e., mid ocean ridge hydrothermal systems).

**Summary, Implications and Conclusions**

Quantitative results of Mo and V uptake by ferrihydrite and their fate after its transformation to hematite showed that more than 90% of Mo and 94% of V were sequestered in the hematite structure after adsorption to ferrihydrite, while 94% of Mo and 100% of V were immobilized after co-precipitation with ferrihydrite.

The Mo and V present in the adsorbed and co-precipitated samples are initially taken up by ferrihydrite as tetrahedrally coordinated molybdate and vanadate, respectively. After the ferrihydrite was transformed to hematite V becomes partially reduced to V(IV). Mo
became incorporated in the hematite structure at mainly distorted octahedral sites. These
distortions may be due to the high temperature and pressure used in the transformation
experiments as well as the fast dehydration, rearrangement during the crystallisation of
hematite from ferrihydrite.

The results from the current study show that at near neutral pH hematite is the main
transformation end-product and that the crystallisation is temperature dependent. At high
temperatures (i.e., 200ºC) hematite is the sole transformation end product whereas at lower
temperatures, goethite is a minor product.

The in-situ and time resolved EDXRD data showed that ferrihydrite transformation to
hematite occurred via 2D phase boundary growth of hematite plates following a
dehydration, rearrangement mechanism. High temperature and higher ionic strength
primarily affected the crystallisation process. The presence of Mo and V had no significant
effect on the crystallisation rate as well as the activation energies. Our kinetic results can
help quantify the time scales of Mo and V sequestration in various environments where
ferrihydrite forms.

We also reported the first rate constants, induction times and activation energies for
three different systems (pure FH, V-FH, Mo-FH) at near neutral pH conditions. These are
important for a plethora of natural systems (i.e., seawater hydrothermal systems, soil and
wastewater remediation processes, etc.,) where scavenging processes play a significant
role in the Mo and V cycles. For example, our data can help estimate the impact of
hydrothermal systems on the Mo and V budget to global ocean. This could be done by
using specific ocean circulation models and assuming that the whole ocean reservoir is
passing through the hydrothermal systems once every 10^3-10^4- years^{82,83} and Mo and V
concentration in the water column is 10 mg L^{-1}^{84} and 2-3 µg L^{-1}^{85}, respectively. As
example, Trefry and Metz, estimated that 10-16% of the riverine V inputs are removed from
seawater by scavenging processes through iron oxides originating from hydrothermal
vents^{17}.

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funding this research.
Supporting information available

Supporting information contains the following figures: (i) XRD analyses of the intermediate transformation product from the off-line ferrihydrite transformation experiments at 160ºC (Figure SI 1); (ii) Progression of hematite (110) and goethite (110) peak areas as function of time for FH-Mo system, at 140ºC and IS 0.7, indicating that small proportions of goethite [GT (110)] is formed besides hematite [HM (110)], (Figure SI 2); (iii) The t₀ (sec) vs. T (C) (Figure SI 3A) and k (s⁻¹) vs. T (C) (Figure SI 3B) profiles of all transformation systems following an exponential trend are plotted to aid the interpolation or extrapolation of any desired temperature, induction time or rate constants; (iv) Arrhenius plots for induction time, t₀ (Figure SI 4A) and rate of growth, k, (Figure SI 4B) of HM crystallisation in the three studied systems; (v) Mo k³ weighted EXAFS spectra for ferrihydrite adsorbed and co-precipitated experiments at different Mo concentrations and standards showing that spectra are alike for all Mo doping concentrations, indicating that Mo did not form specific precipitates or polymerized during co-precipitation/adsorption experiments (Figure SI 5); (vi) Non normalized V-XANES showing beam dehydration effect of V co precipitated fresh ferrihydrite (sample run at room temperature), (Figure SI 6) and (vii) Normalized XANES (Figure 7A), splined K3 weighted EXAFS (Figure 7B) and Fourier transformed of EXAFS (Figure 7C) spectra of V in V-copp- tr sample showing that V bonding environment in transformed sample has changed, but to our best try no sensible model could be fitted, thus we included the data for possible future references. This information is available free of charge via the Internet at http://pubs.acs.org/.

Literature cited


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The effect of Mo and V on the hydrothermal crystallisation of hematite from ferrihydrite - an \textit{in situ} Energy Dispersive X Ray Diffraction and X Ray Absorption Spectroscopy study

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Representative FEG-TEM images of: (A) the starting material, ferrihydrite (FH), (B) intermediate phases consisting of hematite, ferrihydrite and minor goethite (GT) as intermediate and (C) end product, hematite (HM) from the \textit{ex-situ}, pure ferrihydrite transformation experiment at T=160°C;

\textbf{Short synopsis}

The paper discusses the kinetics of the ferrihydrite transformation to hematite near neutral pH and the effect of the ionic strength, molybdenum and vanadium during its transformation. \textit{In situ} Synchrotron Energy Dispersive X-Ray Diffraction technique records the transformation and extracts kinetic rates and apparent activation energies. X-Ray Absorption Spectroscopy gave information about elements bonding environment in ferrihydrite and hematite.
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